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# Prospects for sympathetic cooling of polar molecules: NH with alkali-metal and alkaline-earth atoms – a new hope

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We explore the potential energy surfaces for NH molecules interacting with alkali-metal and alkaline-earth atoms using highly correlated *ab initio* electronic structure calculations. The surfaces for interaction with alkali-metal atoms have deep wells dominated by covalent forces. The resulting strong anisotropies will produce strongly inelastic collisions. The surfaces for interaction with alkaline-earth atoms have shallower wells that are dominated by induction and dispersion forces. For Be and Mg the anisotropy is small compared to the rotational constant of NH, so that collisions will be relatively weakly inelastic. Be and Mg are thus promising coolants for sympathetic cooling of NH to the ultracold regime.

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## I. INTRODUCTION

In recent years there has been growing interest in the production and properties of cold molecules. Possible applications, such as controlled ultracold chemistry [1], quantum information and computing [2], and high-precision measurements of the time-dependence of fundamental ‘constants’ [3–5], make cold molecules extremely interesting across many different fields of physics.

Two main approaches to the production of cold molecules can be distinguished. One approach is based on the coherent formation of ultracold molecules such as Cs<sub>2</sub> or RbCs in trapped ultracold atomic gases [6]. The molecules may be formed either by photoassociation [7] or by Feshbach resonance tuning [8]. They inherit the  $\mu$ K-nK temperatures of the parent ultracold atomic cloud and usually need very little further cooling. Efforts in this area have led to the Bose-Einstein condensation of Feshbach molecules [9–11] and to the transfer of Feshbach molecules to low-lying states [12–14]. There have also been considerable successes in direct photoassociation to produce low-lying states [15–18].

In the other approach, represented for example by Stark deceleration [19, 20] or helium buffer-gas cooling [21], preexisting molecules are decelerated either by external fields or by collisions with other particles and trapped in electrostatic or magnetic traps. The temperature of the resulting molecular cloud is usually in the K-mK region, and therefore new ways for cooling the

molecules further are being sought. A promising route to cooling decelerated molecules down to the  $\mu$ K region is offered by sympathetic cooling.

Sympathetic cooling, in which one species is cooled by thermal contact with another much colder species, was originally developed as a cooling technique for trapped ions [22]. Diatomic [23] and polyatomic [24] molecular ions have been cooled to sub-Kelvin temperatures by thermal contact with cold ions, and sympathetic cooling is expected to be capable of cooling ions of very high mass, including those of biological relevance. Sympathetic cooling has also been successful in producing ultracold neutral atoms of species that are not themselves suitable for evaporative cooling; for example it was used to create the first Bose-Einstein condensates of potassium <sup>41</sup>K [25].

Sympathetic cooling is effective only if the rate of elastic collisions is very large compared to the rate of inelastic collisions. Elastic collisions exchange kinetic energy between molecules and allow thermalization. However, inelastic collisions in which internal energy is converted into relative kinetic energy cause trap loss (if the energy released is greater than the trap depth) or heating (if the energy released is less than the trap depth). Magnetic and electrostatic traps always trap molecules in low-field-seeking states, which are not in their lowest state in the applied field. Since typical traps have depths in the  $\mu$ K or mK range, most inelastic collisions cause trap loss. A commonly stated rule of thumb is that the ratio of elastic to inelastic collision rates must be at least 100 for effective sympathetic cooling.

The obvious *coolants* for the sympathetic cooling of cold molecules are alkali-metal atoms, which can be cooled to ultra-low temperatures on demand. Sympathetic cooling of photoassociated alkali-metal dimers in triplet states by alkali-metal atoms was discussed by

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Cvitaš *et al.* [26, 27], who concluded that the dimers would need to be in their ground rovibrational state because of the unfavorable ratio of inelastic to elastic cross sections in the sub-mK temperature region.

Sympathetic cooling of decelerated molecules by alkali-metal atoms was first considered by Soldán and Hutson [28], who studied the interactions of rubidium atoms with NH molecules. They showed that the  $^2A''$  and  $^4A''$  states of RbNH (bound by covalent and dispersion forces) are crossed by much deeper  $^2A'$  and  $^2A''$  ion-pair states in the energetically allowed region at linear geometries. They concluded that the ion-pair states are likely to have important consequences for the physics of sympathetic cooling of molecules such as CH, NH and OH, because they provide additional mechanisms for inelastic collisions and three-body recombination.

Lara *et al.* [29, 30] subsequently focused on the interaction of OH molecules with ultracold Rb atoms. They developed full sets of coupled potential energy surfaces and carried out quantum collision calculations including spin-orbit and hyperfine coupling. Once again they found a deep ion-pair state ( $^1A'$  for RbOH) that crossed the covalent states at energetically accessible geometries. However, even when the ion-pair state was excluded from the calculation, the anisotropy of the potential for the covalent states was enough to cause strong inelastic collisions that would prevent sympathetic cooling except for atoms and molecules in their absolute ground states. Lara *et al.* concluded in general that (i) light atomic partners are desirable as coolants, because the resulting high centrifugal barriers would suppress many inelastic channels; (ii) weak coupling of the electron to the axis, which occurs in Hund's case b molecules such as NH or CaH, would be beneficial; (iii) the anisotropy of the atom-molecule surface should be comparable to or smaller than the rotational constant of the molecule; and (iv) closed-shell coolants, such as alkaline-earth atoms, may produce more isotropic potential energy surfaces than open-shell coolants, such as alkali-metal atoms. Later a detailed *ab initio* study of 2D adiabatic potential energy surfaces for NH interacting with Rb and Cs atoms was reported by Tacconi *et al.* [31], followed by studies of the quantum dynamics of ultra-low-energy collision processes [32, 33].

Another set of potential coolants for sympathetic cooling are alkaline-earth atoms. Calcium [34] and strontium [35] atoms can be cooled and trapped at temperatures of the order of  $\mu\text{K}$ . Mehlstäubler *et al.* [36] have recently succeeded in cooling magnesium atoms to sub-Doppler temperatures of 500  $\mu\text{K}$ . To our knowledge no attempt has yet been made to cool Be atoms.

Very recently, Żuchowski and Hutson [37] surveyed interactions of  $\text{NH}_3$  molecules with alkali-metal and alkaline-earth atoms. All the systems exhibited deep potential wells (890 to 5100  $\text{cm}^{-1}$ ) when the atom was on the N side of the molecule, and shallow potential wells (100 to 130  $\text{cm}^{-1}$ ) when the atom was on the H side, resulting in very strong anisotropy of the surfaces. Because of this, they concluded that sympathetic cooling of

$\text{NH}_3$  would work only if both species were in their lowest internal states of the symmetry concerned.

In this paper we survey the possibilities for sympathetic cooling of NH molecules, which have very recently been cooled and magnetically trapped at 0.7 K in their ground  $X^3\Sigma^-$  state [38] by buffer-gas cooling. NH molecules in their metastable  $a^1\Delta$  state have also been Stark-decelerated [39] and electrostatically trapped at temperatures of 60-100 mK, and there is a proposal [40] to transfer  $a^1\Delta$  molecules to the  $X^3\Sigma^-$  state. In the present paper we investigate the interactions of  $\text{NH}(X^3\Sigma^-)$  molecules not only with all the relevant alkali-metal (Alk) atoms, but also for the first time with the alkaline-earth (Ae) atoms. We characterize the potential energy surfaces of the covalent and dispersion-bound states of the AlkNH and AeNH systems and locate their conical intersections with the ion-pair states. We show that Be and Mg atoms are promising candidates for sympathetic cooling of  $\text{NH}(X^3\Sigma^-)$  molecules.

## II. METHODS

To facilitate future quantum dynamics calculations, all results are reported in Jacobi coordinates. The intermolecular distance  $R$  is the distance between the alkali-metal or alkaline-earth atom and the center of mass of the NH molecule. The angle  $\theta$  is measured at the center of mass and is zero for linear atom-HN geometries. In all our calculations the NH bond length  $r$  is fixed at the experimentally determined equilibrium value for the free monomer, 1.0367 Å [41].

Supermolecular coupled-cluster calculations were carried out using a single-reference restricted open-shell variant [42] of the coupled cluster method [43] with single, double and non-iterative triple excitations [RCCSD(T)]. All electrons from the “outer-core” orbitals ( $1s$ ,  $2s2p$ ,  $3s3p$ ,  $4s4p$ , and  $5s5p$  for Li and Be, Na and Mg, K and Ca, Rb and Sr, and Cs, respectively) were included in the RCCSD(T) calculations. All the *ab initio* calculations were performed using the MOLPRO package [44].

To describe the interaction between the outer-core and valence electrons, and to reduce basis-set superposition errors, rather large basis sets are needed. We use the correlation-consistent polarized valence quintuple- $\zeta$  (cc-pV5Z) basis sets of Dunning [45] for hydrogen (without the  $g$  functions) and for nitrogen (without the  $h$  functions). Both these basis sets were augmented in an even-tempered manner and used in uncontracted form. For lithium, beryllium, sodium, magnesium, potassium, and calcium atoms, we use the correlation-consistent polarized core-valence quintuple- $\zeta$  cc-pCV5Z basis sets of Iron *et al.* [46], again without the  $h$  functions. The Li, Be, Na, and Mg basis sets were used in fully uncontracted form and those for K and Ca were used partially contracted. These basis sets were also augmented by additional even-tempered diffuse functions. The resulting aug-cc-pCV5Z basis sets

consist of  $(15s, 10p, 8d, 6f, 4g)$ ,  $(20s, 13p, 9d, 7f, 5g)$ , and  $[13s, 12p, 9d, 7f, 5g]$  functions for Li, Na, and K, respectively, and of  $(15s, 9p, 8d, 6f, 4g)$ ,  $(21s, 15p, 9d, 7f, 5g)$ , and  $[13s, 12p, 9d, 7f, 5g]$  functions for Be, Mg, and Ca, respectively. For rubidium, strontium, and cesium, we use the small-core scalar relativistic effective core potentials ECP28MDF and ECP46MDF [47, 48], together with the corresponding valence basis sets. These basis sets were augmented in the even-tempered manner and used in uncontracted form. The resulting basis sets consisted of  $(14s, 11p, 6d, 4f, 2g)$ ,  $(15s, 12p, 7d, 5f, 2g)$ , and  $(13s, 12p, 6d, 4f, 3g)$  primitive Gaussian functions for Rb, Sr, and Cs, respectively.

All interaction energies are calculated with respect to the separated-atom-molecule limit, with both the atom and the molecule in their ground states. The full counterpoise correction of Boys and Bernardi [49] is used to compensate for basis set superposition errors. Optimizations of the counterpoise-corrected dimer interaction energies are performed making use of a general optimization algorithm implemented in MOLPRO.

In order to describe the dispersion-bound state of MgNH for all geometries, we use a version of symmetry-adapted perturbation theory (SAPT) based on a density-functional theory (DFT) description of the monomers. In the SAPT(DFT) method [50] (which we use here only for MgNH), the interaction energy is obtained as a sum of contributions,

$$E_{\text{int}}^{\text{SAPT(DFT)}} = E_{\text{elst}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{disp}}^{(2)} + E_{\text{ind}}^{(2)} + E_{\text{exch-disp}}^{(2)} + E_{\text{exch-ind}}^{(2)}, \quad (1)$$

where  $E_{\text{elst}}^{(1)}$  is the electrostatic energy,  $E_{\text{exch}}^{(1)}$  is the first-order exchange energy,  $E_{\text{disp}}^{(2)}$  and  $E_{\text{ind}}^{(2)}$  are the second-order dispersion and induction energies, and  $E_{\text{exch-disp}}^{(2)}$  and  $E_{\text{exch-ind}}^{(2)}$  are their exchange counterparts. The first-order terms are calculated using Kohn-Sham orbitals, while the dispersion, induction and exchange-induction terms are evaluated using coupled Kohn-Sham density susceptibilities. The exchange-dispersion term is estimated as described in Ref. [50]. However, in Ref. [50] the second-order exchange corrections are given in the so-called  $S^2$  approximation, which neglects terms of third and higher powers in the overlap matrix  $S$ . Since the overlap between Mg and NH is large, we scale the second-order exchange corrections by  $E_{\text{exch}}^{(1)}(S^2)/E_{\text{exch}}^{(1)}$ . This procedure was introduced by Patkowski *et al.* [51] to improve the performance of SAPT for systems with very diffuse monomer densities.

Our SAPT calculations use the PBE0 density functional [52], with augmented correlation-consistent polarized valence quadruple-zeta (aug-cc-pVQZ) basis sets [45, 46] supplemented with bond functions 0.9, 0.3, 0.1  $s$  and  $p$ , 0.6, 0.2  $d$  and  $f$  placed at the midpoint between the Mg atom and the center of mass of NH. The Tozer-Handy asymptotic correction [53] of the exchange-correlation potential is used, with splicing parameters 3.5 and 4.7 Å.

### III. RESULTS AND DISCUSSION

#### A. Alkali-metal atom + NH interactions

In discussing the electronic structure of NH interacting with alkali metals (Alk), it is convenient to begin with linear arrangements. At linear geometries (point group  $C_{\infty v}$ ), there are two covalent states  $^4\Sigma^-$  and  $^2\Sigma^-$ , which correlate with the  $\text{Alk}(^2S) + \text{NH}(^3\Sigma^-)$  dissociation limit. These are crossed by an ion-pair  $^2\Pi$  state, which in a diabatic representation correlates with the  $\text{Alk}^+(^1S) + \text{NH}^-(^2\Pi)$  dissociation limit. (In an adiabatic representation this state changes configuration at a long-range avoided crossing with a higher  $^2\Pi$  state, and in the new configuration it correlates with  $\text{Alk}(^2P) + \text{NH}(^3\Sigma^-)$ ; the ion-pair configuration is then carried up by a cascade of similar avoided crossings until it reaches the  $\text{Alk}^+(^1S) + \text{NH}^-(^2\Pi)$  dissociation limit). At non-linear geometries (point group  $C_s$ ), the  $^4\Sigma^-$  and  $^2\Sigma^-$  states become  $^4A''$  and  $^2A''$  states, while the  $^2\Pi$  state is subject to the Renner-Teller effect and splits into two states with the electron hole either in the triatomic plane ( $^2A'$ ) or perpendicular to it ( $^2A''$ ). In cuts through the potential at fixed N-H distance, the covalent  $^2A''$  and ion-pair  $^2A''$  states avoided-cross at nonlinear geometries but form a conical intersection at linear geometries. In the full three-dimensional picture they form a seam of conical intersections parameterized by the N-H distance.

We consider first the quartet states. The potential curves for the  $^4\Sigma^-$  states at linear Alk-NH geometries are shown in Fig. 1. Results from geometry optimization are given in Table I for both linear configurations.

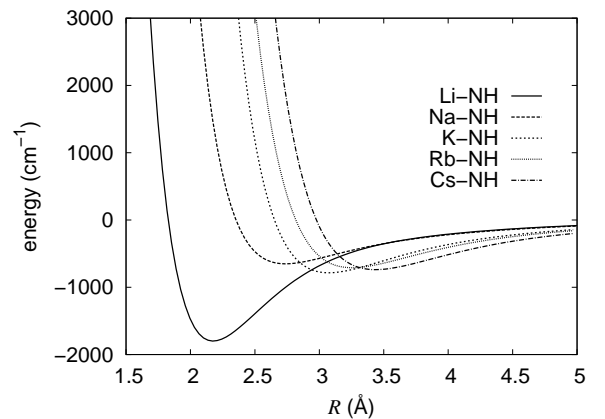


FIG. 1: One-dimensional cuts through the lowest  $^4\Sigma^-$  potential energy surfaces of AlkNH systems at the linear Alk-NH arrangement.

From the viewpoint of sympathetic cooling, the most important feature of the potential surface is its anisotropy. For sympathetic cooling to be successful for internally excited states, we need a potential surface where the anisotropy is small compared to the rotational constant of the monomer ( $B_e = 16 \text{ cm}^{-1}$  for NH). The

TABLE I: Lowest  $^4\Sigma^-$  and  $^2\Pi$  states of linear AlkNH: minima ( $R_{\min}$ ,  $V_{\min}$ ) and crossing points ( $R_x$ ,  $V_x$ ) at different arrangements (Alk-NH, Alk-HN). Energies are given in  $\text{cm}^{-1}$  and distances in  $\text{\AA}$ .

Alk	Alk-NH				Alk-HN			
	$R_{\min}^{\Sigma^-}$	$V_{\min}^{\Sigma^-}$	$R_x$	$V_x$	$R_{\min}^{\Pi}$	$V_{\min}^{\Pi}$	$R_{\min}^{\Sigma^-}$	$V_{\min}^{\Sigma^-}$
Li	2.176	-1799.1	3.09	-600	1.78	-21073	4.658	-115.3
Na	2.737	-651.3	3.21	-470	2.13	-13287	4.872	-98.9
K	3.073	-784.7	3.84	-432	2.42	-14235	5.386	-91.1
Rb	3.254	-709.3	3.99	-412	2.53	-13918	5.521	-87.3
Cs	3.435	-737.9	4.31	-381	2.65	-15116	5.761	-85.0

global minimum for quartet states is at linear Alk-NH geometries for all systems. For LiNH, the well depth at the global minimum is about  $1800 \text{ cm}^{-1}$ , while at the secondary minimum (Li-HN) it is only  $115 \text{ cm}^{-1}$ . The absolute well depths for the other AlkNH systems are a factor of 2 to 3 smaller than for Li-NH, while the depths of the secondary wells are comparable for all the alkali-metal atoms. Nevertheless, for all the AlkNH systems the anisotropy is very large compared to the rotational constant of NH. Because of this, collisions that take place on the quartet surfaces are likely to be strongly inelastic.

The large anisotropy of the AlkNH quartet surfaces results from strong  $sp$  mixing of the alkali-metal orbitals in the Alk-NH arrangement. Such mixing is much weaker in the Alk-HN arrangement. To quantify this we have performed Mulliken population analysis [54]. The strongest effect is observed for LiNH, where the partial occupancy of the valence  $p_z$  orbital is 0.086 in the Li-NH arrangement compared to 0.004 in the Li-HN arrangement. The  $p_z$  occupancy for Alk-NH arrangements decreases down the periodic table: Na 0.068, K 0.037, Rb 0.027 and Cs 0.021. This hybridization tendency is similar to that found for the alkali-metal trimers in the quartet states [55].

The present calculations give a quartet well depth for RbNH that is about 12% deeper than the value of  $78 \text{ meV}$  ( $630 \text{ cm}^{-1}$ ) obtained by Soldán and Hutson [28] using multireference configuration interaction (MRCI) calculations. The present work used RCCSD(T) calculations, which give a better treatment of dispersion effects, and also used much larger basis sets. Our well depths are also substantially deeper than those reported for Rb-NH and Cs-NH by Tacconi *et al.* [31] using methods and basis sets similar to those of Ref. [28].

For all the Alk-NH systems there are also covalent states of  $^2\Sigma^-$  symmetry ( $^2A''$  at bent geometries) and an ion-pair state of  $^2\Pi$  symmetry ( $^2A'$  and  $^2A''$  at bent geometries). As described above, there is an avoided crossing between the two  $^2A''$  states. Table I gives the equilibrium positions and well depths of the  $^2\Pi$  states for Alk-NH geometries, and it may be seen that for all systems the ion-pair well is more than  $13000 \text{ cm}^{-1}$  deep. The potential curve for the  $^2\Sigma^-$  state cannot be obtained from RCCSD(T) calculations, but it is qualitatively similar to that for the  $^4\Sigma^-$  state in the long-range region [28]. Table I includes the position and energy of the crossing

point between the  $^4\Sigma^-$  and  $^2\Pi$  curves, and it may be seen that the crossing is always outside the minimum of the  $\Sigma$  state. Because of this, the lowest adiabatic surface of either  $^2A'$  or  $^2A''$  symmetry always has a very deep well of ion-pair character. This well is strongly anisotropic, so that any collision that samples the doublet surfaces is likely to be strongly inelastic.

In conclusion, it appears that both the doublet and quartet surfaces of Alk-NH systems have sufficient anisotropy that inelastic collisions will dominate whenever they are energetically allowed. Sympathetic cooling of NH molecules by alkali-metal atoms is thus unlikely to be effective unless both the atom and the molecule are in their absolute ground state in any applied field.

## B. Alkaline-earth atom + NH interactions

The potential energy surfaces for alkaline-earth atoms (Ae) interacting with NH are substantially different from those for AlkNH systems. At linear geometries, there is one dispersion-bound state,  $^3\Sigma^-$ , which correlates with the  $\text{Ae}(^1S) + \text{NH}(^3\Sigma^-)$  dissociation limit. This state is crossed by ion-pair  $^3\Pi$  and  $^1\Pi$  states, which in a diabatic representation correlate with the  $\text{Ae}^+(^2S) + \text{NH}^-(^2\Pi)$  dissociation limit. At non-linear geometries (point group  $C_s$ ), the  $^3\Sigma^-$  state becomes a  $^3A''$  state, and the  $^3\Pi$  state is subject to the Renner-Teller effect and splits into two states with the electron hole either in the triatomic plane ( $^3A'$ ) or perpendicular to it ( $^3A''$ ). In cuts at fixed NH bond length, the dispersion-bound  $^3A''$  and ion-pair  $^3A''$  states form a conical intersection at linear geometries, while in the full three-dimensional picture they form a seam of conical intersections parameterized by the N-H distance.

The counterpoise-corrected equilibrium distances and well depths for AeNH systems are shown in Table II for both Ae-NH and Ae-HN linear geometries. The corresponding potential curves are shown in Figs. 2 and 3 for Ae-NH and Ae-HN geometries, respectively. It may be seen that the anisotropy of the dispersion-bound state is considerably smaller for the alkaline-earth atoms than for the alkali-metal atoms. However, for Ca and Sr the difference between the well depths at the two linear geometries ( $60.4$  and  $184.6 \text{ cm}^{-1}$ , respectively) is still several times the NH rotational constant ( $B_e = 16 \text{ cm}^{-1}$ ). For

Be and Mg, by contrast, the difference is only  $10.5 \text{ cm}^{-1}$  and  $3.6 \text{ cm}^{-1}$ , respectively, which is *smaller* than the NH rotational constant. The difference may be understood in terms of the smaller *s-p* excitation energies for Ca and Sr (1.9 and 1.8 eV, respectively) compared to those of Be and Mg (both 2.7 eV).

Another important feature is the position of the crossing between the dispersion-bound  $^3\Sigma^-$  state and the ion-pair  $^3\Pi$  states. These are also tabulated in Table II and shown in Figs. 2 and 3. For Be-NH and Mg-NH the crossing occurs fairly high on the repulsive wall of the  $^3\Sigma^-$  state, while for Ca-NH and Sr-NH it occurs at negative energies (in the potential well). This may be crucial for collisional properties. If the crossing is located at negative energies, as for Ca-NH and Sr-NH, the deep, strongly anisotropic ion-pair well may be accessed in low-energy collisions and is likely to result in strong inelasticity. On the other hand, if the crossing occurs at a high energy in a classically inaccessible region, as for Be-NH and Mg-NH, the deep ion-pair well is accessible only by tunneling through a barrier and may not have a strong effect on collisions.

For Ae-HN geometries, shown Table II, the crossing occurs high on the repulsive wall for all the AeNH systems.

### C. Mg-NH interaction potential

As shown above, the BeNH and MgNH systems have potential energy surfaces that appear promising for sympathetic cooling. However, Mg has been successfully laser-cooled [36] whereas Be has not. We therefore focus in this section on developing a complete potential energy surface for interaction of Mg with  $\text{NH}(^3\Sigma^-)$ .

For bent geometries near the conical intersection, the two lowest triplet states of  $A''$  symmetry are near-degenerate. Under these circumstances single-reference coupled-cluster calculations are inappropriate. One alternative, which we have previously applied for RbOH [29, 30], is to carry out multireference configuration interaction calculations including single and double excitations (MR-CISD). However, for MgNH the contribution from triple excitations is extremely large: for example, the well depths of the linear  $^3\Sigma^-$  state is underestimated by 40% in RCCSD calculations. Because of this, we use SAPT(DFT) calculations to study nonlinear configurations of MgNH. It has recently been demonstrated [50, 51] that SAPT(DFT) gives reasonably good results for  $\text{Mg}_2$ ,  $\text{NH-He}$  and  $\text{MgHe}$ , and the polarizabilities and Van der Waals coefficients for  $\text{Mg}_2$  are reproduced with an accuracy of a few percent. A further advantage of the perturbation theory is that, by starting from zeroth-order wavefunctions corresponding to neutral monomers, we produce diabatic potential energy surfaces corresponding to neutral Mg-NH without contamination from ion-pair states.

Fig. 4 shows the potential energy surface for Mg-NH

obtained from SAPT(DFT) calculations. There are minima at both linear geometries and a saddle point between them, with a barrier of only  $24 \text{ cm}^{-1}$ . The agreement between CCSD(T) and SAPT(DFT) methods for linear configurations is very good for the Mg-NH geometry, where SAPT(DFT) overestimates the RCCSD(T) well depth by 6%. The agreement is slightly worse for the Mg-HN geometry, where SAPT(DFT) underestimates the well depth by 9% (see Fig. 5).

The ion-pair state does not reach negative energies until distances  $R < 2.6 \text{ \AA}$ . The dispersion-bound state is strongly repulsive at such distances. We have carried out multireference self-consistent field (MCSCF) calculations of the two states of  $^3A''$  symmetry in the region of their avoided crossing for a range of angles using a cc-pVQZ basis set [45, 46]. The lowest barrier for crossing onto the ion-pair state occurs for an angle  $\sim 110^\circ$  at a distance of  $R \sim 2.4 \text{ \AA}$  and an energy of  $+2200 \text{ cm}^{-1}$  with respect to the atom-molecule threshold. The singlet ion-pair state is about  $700 \text{ cm}^{-1}$  shallower than the triplet near its equilibrium geometry and will therefore cross the dispersion-bound state at even higher energies.

The collision energies of importance to sympathetic cooling are in the range between  $1 \text{ }\mu\text{K}$  and  $100 \text{ mK}$  ( $0.06 \text{ cm}^{-1}$ ). At such energies we believe that the barrier separating the wells of the ion-pair and dispersion-bound states is wide and high enough to neglect the conversion from  $\text{MgNH}$  to  $\text{Mg}^+\text{NH}^-$  and to perform collision calculations only on the dispersion-bound surface.

## IV. CONCLUSIONS

In this paper we have presented an overview of the interaction potentials of alkali-metal and alkaline-earth atoms with NH molecules in their ground  $^3\Sigma^-$  state. The interaction potentials of quartet states of  $\text{AlkNH}$  systems are strongly anisotropic, with deep wells at  $\text{Alk-NH}$  geometries. The bonding in the well region involves strong mixing of the *s* and *p* orbitals of the alkali-metal atom and is thus covalent in nature. For geometries close to  $\text{Alk-NH}$  configurations the quartet states are crossed by ion-pair doublet states in the energetically accessible region. Because of the presence of the ion-pair state, the lowest doublet adiabatic potential energy surface has a very deep well.

For alkaline-earth atoms the interaction potentials are much shallower and less anisotropic, especially for BeNH and MgNH. The *sp* mixing is much weaker and the bonding is dominated by induction and dispersion forces. For MgNH the anisotropy is comparable to or smaller than the rotational constant of NH,  $B_e$ . For CaNH and SrNH the anisotropy is rather larger, of the order of  $4B_e$  for CaNH and  $11B_e$  for SrNH. The relatively weak anisotropy raises the hope that alkaline earth atoms could be used for sympathetic cooling of NH molecules.

The dispersion-bound  $^3\Sigma^-$  states of AeNH systems are crossed by singlet and triplet ion-pair states  $^1\Pi$  and  $^3\Pi$ .

TABLE II: Lowest  $^3\Sigma^-$  and  $^3\Pi$  states of linear AeNH: minima ( $R_{\min}$ ,  $V_{\min}$ ) and crossing points ( $R_x$ ,  $V_x$ ) at different arrangements (Ae-NH, Ae-HN). Energies are given in  $\text{cm}^{-1}$  and distances in  $\text{\AA}$ .

Ae	Ae-NH				Ae-HN			
	$R_{\min}^{\Sigma}$	$V_{\min}^{\Sigma}$	$R_x$	$V_x$	$R_{\min}^{\Pi}$	$V_{\min}^{\Pi}$	$R_{\min}^{\Sigma}$	$V_{\min}^{\Sigma}$
Be	3.995	-84.5	2.30	2390	1.55	-20240	4.301	-95.4
Mg	4.157	-106.5 <sup>a</sup>	2.59	1510	1.95	-10120	4.636	-103.0 <sup>b</sup>
Ca	3.963	-165.7	3.19	-146	2.19	-17041	5.149	-104.5
Sr	3.175	-286.4	3.39	-267	2.32	-16734	5.340	-101.8

<sup>a</sup> $E_{\text{int}}^{\text{SAPT(DFT)}} = -113.4 \text{ cm}^{-1}$  and corresponding  $R_{\min}^{\Sigma} = 4.24 \text{ \AA}$

<sup>b</sup> $E_{\text{int}}^{\text{SAPT(DFT)}} = -91.7 \text{ cm}^{-1}$  and corresponding  $R_{\min}^{\Sigma} = 4.74 \text{ \AA}$

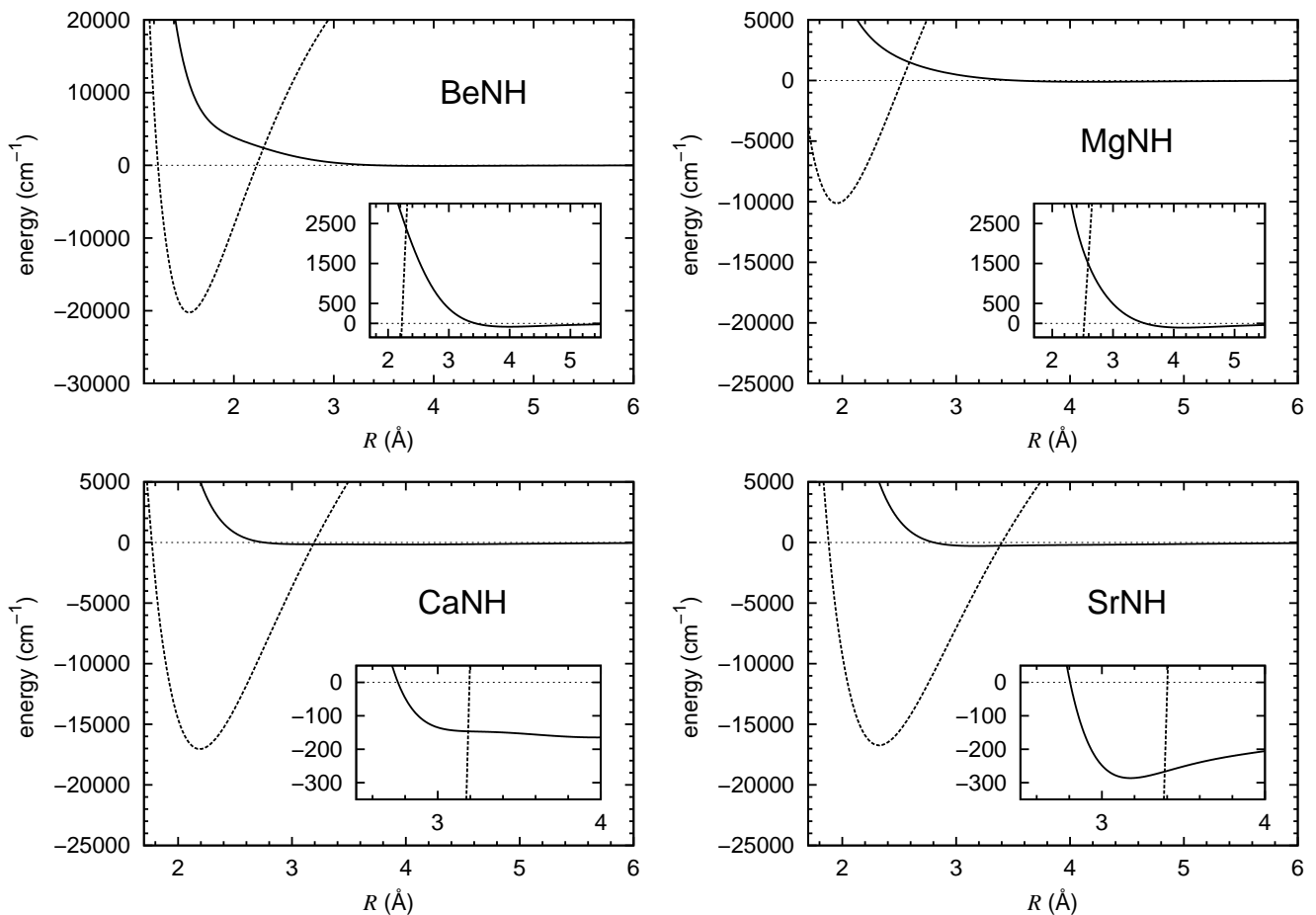


FIG. 2: One-dimensional cuts through the lowest  $^3\Sigma^-$  (full) and  $^3\Pi$  (dashed) potential energy surfaces of AeNH systems at the linear Ae-NH arrangement. For clarity, the region near the crossing of the dispersion-bound and ion-pair states is magnified.

At nonlinear geometries the  $^3\Sigma^-$  state becomes  $^3A''$  and there is a component of the  $^3\Pi$  state of the same symmetry. The absolute minimum thus has ion-pair character in all cases. For CaNH and SrNH the ion-pair state crosses the dispersion-bound state in the energetically accessible region, so that the adiabatic potential energy surfaces have a single-minimum structure with a deep potential well and strong anisotropy. For BeNH and MgNH, however, the crossing occurs on the repulsive wall of the potential of the dispersion-bound state and the deep ion-

pair well is likely to be inaccessible in low-energy collisions. We have calculated a full 2-dimensional potential energy surface for MgNH and verified that the crossing occurs on the repulsive wall at all geometries.

The BeNH and MgNH systems are thus promising candidates for sympathetic cooling. In future work we will carry out collision calculations on MgNH to explore this further.

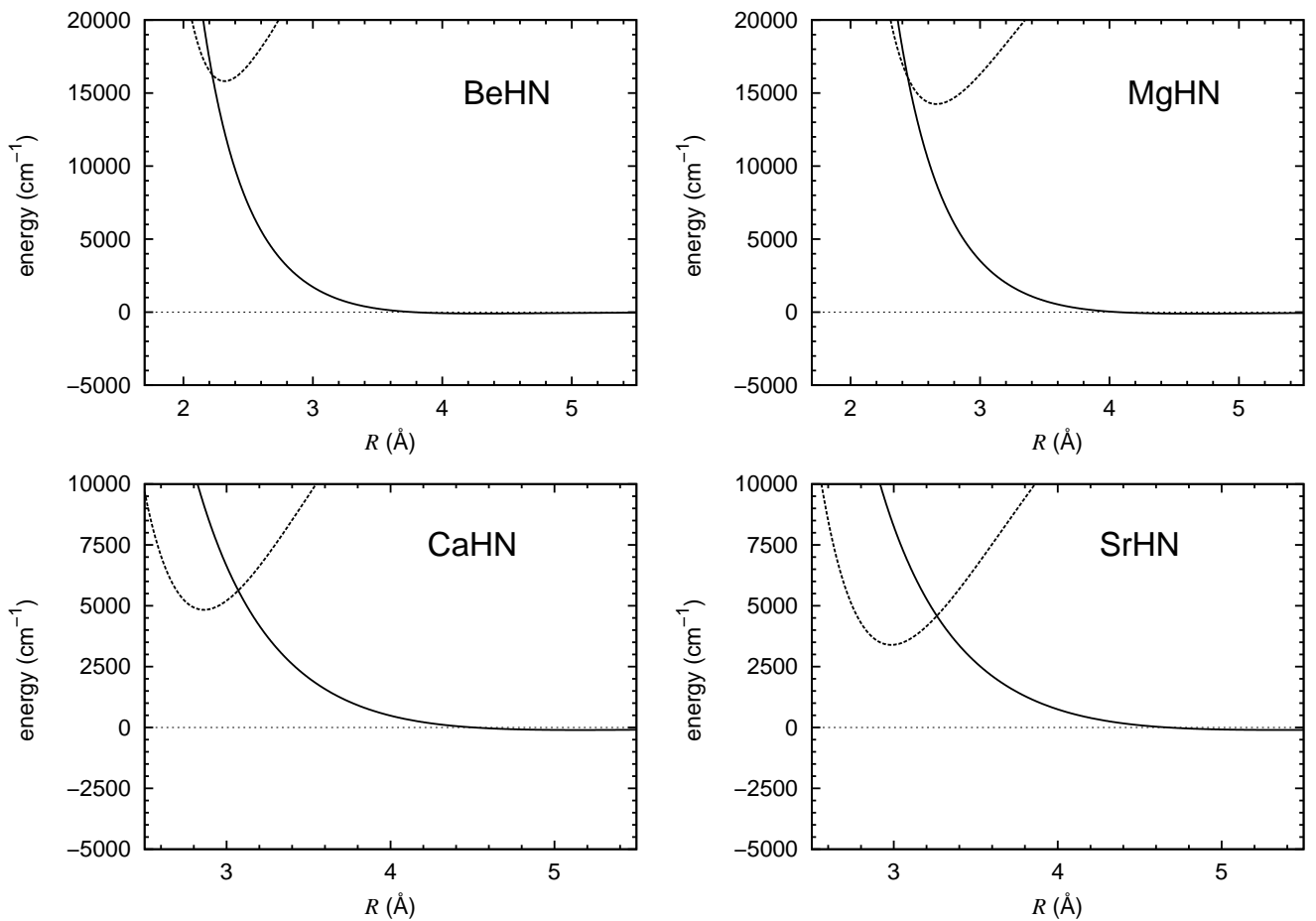


FIG. 3: One-dimensional cuts through the lowest  $^3\Sigma^-$  (full) and  $^3\Pi$  (dashed) potential energy surfaces of AeNH systems at the linear Ae-HN arrangement.

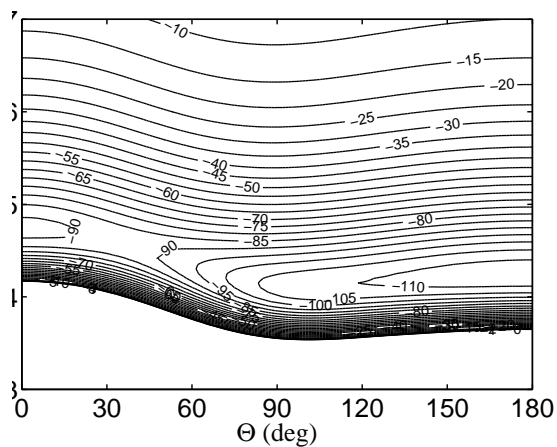


FIG. 4: Contour plot of the potential energy surface for the dispersion-bound state of Mg-NH, from SAPT(DFT) calculations. (in  $\text{cm}^{-1}$ ).

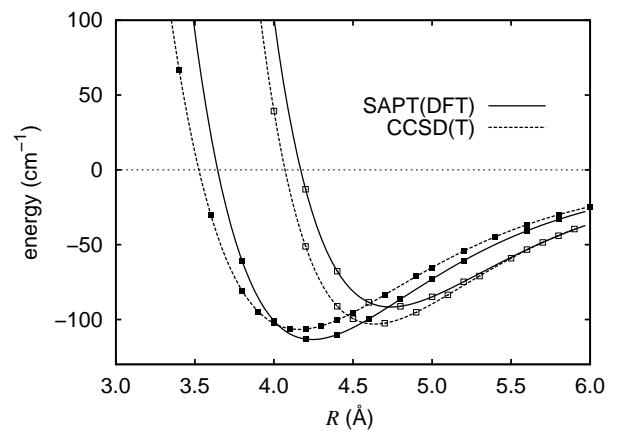


FIG. 5: Comparison of SAPT(DFT) and CCSD(T) interaction energies for linear MgNH configurations. Lines with black squares refer to Mg-NH geometries, while empty squares refer to Mg-HN geometries.



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